1.7 Solving Equilibrium Problems—Type II

In this section, techniques will be developed for solving problems where the given information is

1. The initial concentrations, and
2. The value of K.

Sample Exercise 1.7

At 700 K, carbon monoxide reacts with water to form carbon dioxide and hydrogen:

$$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$$

The equilibrium constant for this reaction at 700 K is 5.10.

Consider an experiment in which 1.00 mol of $CO(g)$ and 1.00 mol of $H_2O(g)$ are mixed together in a 1.00 L flask at 700 K. Calculate the concentrations of all species at equilibrium.

Solution

The first step in solving equilibrium problems is to write the equilibrium expression. In this case,

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]} = 5.10$$

Next write down the initial concentrations:

$$[CO]_0 = \frac{1.00\text{ mol}}{1.00\text{ L}} = 1.00\text{ mol/L}$$

$$[H_2O]_0 = \frac{1.00\text{ mol}}{1.00\text{ L}} = 1.00\text{ mol/L}$$

$$[CO_2]_0 = 0$$

$$[H_2]_0 = 0$$

It is clear that for this system to reach equilibrium it must proceed to the right (some CO_2 and H_2 will be formed by consuming some CO and H_2O). The key question is: How much CO_2 and H_2 will form as the system comes to equilibrium?

To consider this question systematically, use algebraic techniques. As is customary in algebra, assign the symbol x to the unknown quantity. In this problem, the amounts of CO_2 and H_2 formed to reach equilibrium are the unknown quantities. Let x equal the number of moles per liter of CO_2 formed to reach equilibrium.

If x mol/L of CO_2 have been formed, how much H_2 will be present? Since CO_2 and H_2 are formed in equal amounts, x mol/L of H_2 will be formed.

How much CO is consumed to form x mol/L of CO_2 and H_2? Since all the coefficients in the balanced equation are 1, x mol/L of CO are consumed, as well as x mol/L of H_2O. Thus, at equilibrium, the concentrations of reactants and products present are

Concentration of substance at equilibrium = concentration initially present + change

$$[CO] = [CO]_0 - x = 1.00\text{ mol/L} - x\text{ mol/L}$$

$$[H_2O] = [H_2O]_0 - x = 1.00\text{ mol/L} - x\text{ mol/L}$$

$$[CO_2] = [CO_2]_0 + x = 0 + x\text{ mol/L}$$

$$[H_2] = [H_2]_0 + x = 0 + x\text{ mol/L}$$

The ratio of these equilibrium concentrations must give the equilibrium constant:

$$K = 5.10 = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(x)(x)}{(1.00 - x)(1.00 - x)} = \frac{x^2}{(1.00 - x)^2}$$

Taking the square root of both sides gives

$$\frac{x}{1 - x} = \sqrt{5.10} = 2.26$$

$$x = 2.26 - 2.26x$$

$$3.26x = 2.26$$

$$x = 0.69 \text{ mol/L}$$

Thus the equilibrium concentrations are

$$[CO_2] = x = 0.69 \text{ mol/L}$$

$$[H_2] = x = 0.69 \text{ mol/L}$$

$$[H_2O] = 1.00 - x = 0.31 \text{ mol/L}$$

$$[CO] = 1.00 - x = 0.31 \text{ mol/L}$$

TEST 1.7 Consider the reaction at 700 K:

$$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g) \qquad K = 5.10$$

Calculate the equilibrium concentrations of all reactants and products in an experiment where 3.00 mol of $CO(g)$ and 3.00 mol of $H_2O(g)$ are mixed in a 1.00 L flask at 700 K.

Sample Exercise 1.8 Consider the reaction

$$H_2(g) + F_2(g) \rightleftarrows 2HF(g)$$

at a temperature where $K = 1.15 \times 10^2$. In an experiment, 3.00 mol of H_2 and 6.00 mol of F_2 are mixed in a 3.00 L container. Calculate the equilibrium concentrations of H_2, F_2, and HF.

Solution

The equilibrium constant expression is

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]}$$

The initial concentrations are

$$[H_2]_0 = \frac{3.00 \text{ mol}}{3.00 \text{ L}} = 1.00 \text{ mol/L}$$

$$[F_2]_0 = \frac{6.00 \text{ mol}}{3.00 \text{ L}} = 2.00 \text{ mol/L}$$

$$[HF]_0 = 0$$

Now define the change required to reach equilibrium. In this case, since no HF is initially present, some H_2 and F_2 will react to form HF.

Let x be the concentration of H_2 consumed. Using the stoichiometry of the reaction,

$$H_2 \quad + \quad F_2 \quad \longrightarrow \quad 2HF$$

$$x\ \text{mol/L}\ H_2 + x\ \text{mol/L}\ F_2 \longrightarrow 2x\ \text{mol/L HF}$$

These are the changes in concentration required to reach equilibrium.

Now write the equilibrium concentrations:

$$[H_2] = [H_2]_0 + \text{change} = 1.00\ \text{mol/L} - x\ \text{mol/L}$$

$$[F_2] = [F_2]_0 + \text{change} = 2.00\ \text{mol/L} - x\ \text{mol/L}$$

$$[HF] = [HF]_0 + \text{change} = 0 + 2x\ \text{mol/L}$$

To solve for the value of x, substitute these concentrations in the equilibrium expression:

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2x)^2}{(1.00 - x)(2.00 - x)}$$

Note that this expression cannot be solved by taking the square root of both sides, since the denominator is not a perfect square. To solve for x, first multiply out the terms:

$$1.15 \times 10^2 = \frac{(2x)^2}{(1.00 - x)(2.00 - x)} = \frac{4x^2}{2.00 - 3.00x + x^2}$$

$$(1.15 \times 10^2)(2.00 - 3.00x + x^2) = 4x^2$$

$$(2.30 \times 10^2) - (3.45 \times 10^2)x + (1.15 \times 10^2)x^2 = 4x^2$$

Subtracting $4x^2$ from both sides and rearranging gives

$$(1.11 \times 10^2)x^2 - (3.45 \times 10^2)x + (2.30 \times 10^2) = 0$$

This is a quadratic equation, which has the general form

$$ax^2 + bx + c = 0$$

The solutions to an equation of this type can be obtained from the formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where a and b are the coefficients of x^2 and x, respectively, and c is the constant in the general equation. In the quadratic equation above,

$$a = 1.11 \times 10^2$$

$$b = -3.45 \times 10^2$$

$$c = 2.30 \times 10^2$$

Thus

$$x = \frac{-(-3.45 \times 10^2) \pm \sqrt{(-3.45 \times 10^2)^2 - (4)(1.11 \times 10^2)(2.30 \times 10^2)}}{2(1.11 \times 10^2)}$$

$$= \frac{3.45 \times 10^2 \pm \sqrt{1.19 \times 10^5 - 1.02 \times 10^5}}{2.22 \times 10^2}$$

$$= \frac{3.45 \times 10^2 \pm \sqrt{1.7 \times 10^4}}{2.22 \times 10^2} = \frac{3.45 \times 10^2 \pm 1.30 \times 10^2}{2.22 \times 10^2}$$

The two roots are

$$x = \frac{3.45 \times 10^2 + 1.30 \times 10^2}{2.22 \times 10^2} = 2.14 \text{ mol/L}$$

$$x = \frac{3.45 \times 10^2 - 1.30 \times 10^2}{2.22 \times 10^2} = 0.968 \text{ mol/L}$$

In this situation, there is only one correct value of x (there is only one equilibrium position which results from these initial concentrations). Which value of x is correct?

The correct value can be chosen by looking at the equilibrium concentrations. Since

$$[H_2] = 1.00 - x$$

the value $x = 2.14$ gives a negative number for the concentration of H_2. This is physically impossible. Therefore, $x = 0.968$ mol/L must be the correct root.

Now compute the equilibrium concentrations:

$$[H_2] = 1.00 - x = 1.00 - 0.968 = 3.2 \times 10^{-2} \text{ mol/L}$$

$$[F_2] = 2.00 - x = 2.00 - 0.968 = 1.03 \text{ mol/L}$$

$$[HF] = 2x = 2(0.968) = 1.94 \text{ mol/L}$$

After solving the quadratic equation, it is wise to check the correctness of the computed concentrations. This can be done by substituting into the equilibrium constant expression:

$$\frac{[HF]^2}{[H_2][F_2]} = \frac{(1.94)^2}{(3.2 \times 10^{-2})(1.03)} = 114$$

The given value of K is 115. Thus there is agreement within the error caused by round-off, and the calculated concentrations are shown to be correct.

TEST 1.8 Consider the reaction

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

at a temperature where $K = 60.0$. In an experiment, 1.50 mol of H_2 and 2.50 mol of I_2 are placed in a 1.00 L flask. Calculate the equilibrium concentrations of H_2, I_2, and HI.

Next, problems in which none of the initial concentrations are zero will be considered. To solve these problems,

1. Calculate the reaction quotient, Q.
2. Determine the direction of the shift to equilibrium.
3. Define the change required to reach equilibrium.
4. Calculate the equilibrium concentrations.

Sample Exercise 1.9 Consider the reaction

$$2HF(g) \rightleftarrows H_2(g) + F_2(g)$$

where $K = 1.0 \times 10^{-2}$ at some very high temperature. In an experiment, 5.00 mol of HF(g), 0.500 mol of H_2(g), and 0.750 mol of F_2(g) are mixed in a 5.00 L flask and allowed to react to equilibrium.

A. Write the equilibrium constant expression.

Solution

$$K = \frac{[H_2][F_2]}{[HF]^2} = 1.0 \times 10^{-2}$$

B. Calculate the initial concentrations.

Solution

$$[HF]_0 = \frac{5.00\text{ mol}}{5.00\text{ L}} = 1.00\text{ mol/L}$$

$$[F_2]_0 = \frac{0.750\text{ mol}}{5.00\text{ L}} = 0.150\text{ mol/L}$$

$$[H_2]_0 = \frac{0.500\text{ mol}}{5.00\text{ L}} = 0.100\text{ mol/L}$$

C. Calculate Q and determine in which direction the reaction will shift to reach equilibrium.

Solution

$$Q = \frac{[F_2]_0[H_2]_0}{[HF]_0^2} = \frac{(0.150)(0.100)}{(1.00)^2} = 1.50 \times 10^{-2}$$

Q is larger than K. To come to equilibrium, the system must shift to the left (i.e., the numerator must get smaller and the denominator larger).

D. Define the change required to reach equilibrium.

Solution

Let x be the mol/L of H_2 consumed to reach equilibrium. Note that x mol/L of F_2 will also be consumed and that $2x$ mol/L of HF will be formed.

E. Define the equilibrium concentrations of all species.

Solution

$$[H_2] = [H_2]_0 - x = 0.100 - x$$

$$[F_2] = [F_2]_0 - x = 0.150 - x$$

$$[HF] = [HF]_0 + 2x = 1.00 + 2x$$

F. Solve for x and calculate the equilibrium concentrations.

Solution

$$1.00 \times 10^{-2} = \frac{[H_2][F_2]}{[HF]^2} = \frac{(0.100 - x)(0.150 - x)}{(1.00 + 2x)^2}$$

Multiplying and collecting terms gives

$$0.960x^2 - 0.290x + 5.00 \times 10^{-3} = 0$$

This is a quadratic equation where

$$a = 0.960$$

$$b = -0.290$$

$$c = 5.00 \times 10^{-3}$$

Use the quadratic formula to solve for x.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(-0.290) \pm \sqrt{(-0.290)^2 - 4(0.960)(5.00 \times 10^{-3})}}{2(0.960)}$$

Solving for x gives the roots

$$x = 0.284 \text{ mol/L}$$

$$x = 0.018 \text{ mol/L}$$

Since $[H_2] = 0.100 - x$, the root $x = 0.284$ cannot be correct. Thus

$$x = 0.018 \text{ mol/L}$$

is the appropriate root. The equilibrium concentrations are

$$[H_2] = [H_2]_0 - x = 0.100 \text{ mol/L} - 0.018 \text{ mol/L} = 0.082 \text{ mol/L}$$

$$[F_2] = [F_2]_0 - x = 0.150 \text{ mol/L} - 0.018 \text{ mol/L} = 0.132 \text{ mol/L}$$

$$[HF] = [HF]_0 + 2x = 1.00 \text{ mol/L} + 2(0.018 \text{ mol/L}) = 1.04 \text{ mol/L}$$

TEST 1.9 Consider the reaction

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g) \qquad K = 5.0 \times 10^{-2} \text{ mol/L at } 240°C.$$

In an experiment, 0.200 mol of $PCl_5(g)$, 0.500 mol of $PCl_3(g)$, and 0.300 mol of $Cl_2(g)$ are mixed in a 2.00 L vessel.

A. Calculate the initial concentrations.
B. Calculate Q using these initial concentrations.
C. Which way does the system adjust to reach equilibrium?
D. Define the change needed to reach equilibrium in terms of x.
E. Define the equilibrium concentrations in terms of x.
F. Substitute the equilibrium values into the equilibrium expression and solve for x.
G. Calculate the equilibrium concentrations of $PCl_5(g)$, $PCl_3(g)$, and $Cl_2(g)$.

Calculations Involving Pressures

Sample Exercise 1.10 Consider the reaction

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

at a temperature where $K_p = 0.131$ atm. A flask initially contains $N_2O_4(g)$ at 1.000 atm pressure. Calculate the pressures of $NO_2(g)$ and $N_2O_4(g)$ at equilibrium.

Solution

Note that the usual steps are followed for this exercise but are condensed:

$$N_2O_4(g) \rightleftarrows 2NO_2(g) \qquad K_p = \frac{P_{NO_2}{}^2}{P_{N_2O_4}} = 0.131$$

Initial Pressures		*Equilibrium Pressures*
$P_{N_2O_4}{}^0 = 1.000$ atm	$\xrightarrow[\text{of } NO_2 \text{ to come to equilibrium}]{\text{Let } x \text{ atm of } N_2O_4 \text{ react to form } 2x \text{ atm}}$	$P_{N_2O_4} = 1.000 - x$
$P_{NO_2}{}^0 = 0$		$P_{NO_2} = 2x$

$$0.131 = K_p = \frac{P_{NO_2}{}^2}{P_{N_2O_4}} = \frac{(2x)^2}{(1.000 - x)}$$

Multiplying and collecting terms gives the quadratic equation

$$4x^2 + 0.131x - 0.131 = 0$$

where $a = 4$, $b = 0.131$, and $c = -0.131$. Use of the quadratic formula gives

$$x = 0.165 \text{ atm (and an } \textit{extraneous} \text{ root, } x = -0.198 \text{ atm)}$$

The equilibrium pressures are

$$P_{N_2O_4} = 1.000 - x = 0.835 \text{ atm}$$

$$P_{NO_2} = 2x = 2(0.165) = 0.330 \text{ atm}$$

1.8 Le Châtelier's Principle

A system will remain at equilibrium unless disturbed in some way. Since certain types of "disturbances" often occur, it is useful to be able to predict in which direction the position of the equilibrium will shift when disturbed. This prediction may be made in terms of Le Châtelier's Principle:

If a stress is applied to a system at equilibrium, the position of the equilibrium shift in the direction which reduces the stress.

Several types of stresses (disturbances) will be considered:

1. Addition or removal of reactants or products.
2. Change in pressure by
   (a) Change in volume.
   (b) Addition of an inert gas.
3. Change in temperature.

The effects of these stresses are explained in the following exercise.

Sample Exercise 1.11 A 1.000 L vessel contains $N_2(g)$, $H_2(g)$, and $NH_3(g)$ at equilibrium. The reaction is exothermic (heat is produced):

$$3H_2(g) + N_2(g) \rightleftarrows 2NH_3(g)$$

The concentrations are

$$[N_2] = 0.921 \text{ mol/L}$$

$$[H_2] = 0.763 \text{ mol/L}$$

$$[NH_3] = 0.158 \text{ mol/L}$$

A. Predict the effect on the equilibrium position of adding 1.000 mol of H_2.

Solution

The stress is the added H_2 which, according to Le Châtelier's Principle, will cause the position of the equilibrium to shift to the right, consuming H_2 and relieving the stress. This effect can be rationalized in terms of the reaction quotient. Immediately after addition of H_2, the system is no longer at equilibrium. The concentrations at that point can be considered to be initial concentrations:

$$[N_2]_0 = 0.921 \text{ mol/L}$$
$$[NH_3]_0 = 0.158 \text{ mol/L}$$
$$[H_2]_0 = 0.763 \text{ mol/L} + 1.000 \text{ mol/L}$$
$$Q = \frac{[NH_3]_0^{\,2}}{[N_2]_0[H_2]_0^{\,3}}$$

Since $[H_2]_0$ is greater than the concentration of H_2 in the system formerly at equilibrium, Q will be smaller than K, and the system will adjust to the right.

Experimental results confirm this conjecture. The new equilibrium concentrations show an increase in $[NH_3]$ and a decrease in $[N_2]$. The details are summarized below.

Equilibrium Position I		*Equilibrium Position II*
$[NH_3] = 0.158$ mol/L	$\xrightarrow[\text{1.000 mol } H_2]{\text{add}}$	$[NH_3] = 0.378$ mol/L
$[N_2] = 0.921$ mol/L		$[N_2] = 0.811$ mol/L
$[H_2] = 0.763$ mol/L		$[H_2] = 1.433$ mol/L

Note that this shows the shift to the right (toward NH_3).

B. Predict the effect of adding 1.000 mol of $NH_3(g)$ to the system.

Solution

The equilibrium position will shift to the left, since the stress is applied to the right side of the equation (Q will be larger than K).

C. Predict the effect of suddenly halving the volume (increasing the pressure).

Solution

The stress applied is reducing the volume. To relieve this stress, the system will shift in a direction that reduces its own volume. This can be done by a shift to the right, since the right side of the equation involves fewer molecules of gas and thus lower volume.

D. Predict the effect of increasing pressure by adding He(g). Assume ideal behavior for all gases.

Solution

There will be no effect on the equilibrium position. Ideal gas molecules have negligible volumes. Thus the addition of He(g) does not change the volume, and since He is not involved in the reaction, the concentrations of reacting molecules are unaffected. The equilibrium position remains unchanged.

E. Predict the effect of increasing the temperature.

Solution

The equilibrium will shift to the left.

This situation is more complicated than those discussed above because the *value of K* changes with temperature. The other disturbances that have been considered (addition or removal of reactants or products and change in pressure) *do not* change the value of K. However Le Châtelier's Principle can be used in this case by considering heat to be a reactant or product. The reaction is exothermic, which can be shown by treating heat as a product:

$$3H_2(g) + N_2(g) \rightleftarrows 2NH_3(g) + \text{heat}$$

The temperature is increased by adding heat. Le Châtelier's Principle predicts that the equilibrium position will shift to the left, consuming some of the added heat.

Note that this shift to the left will decrease $[NH_3]$ and increase $[H_2]$ and $[N_2]$ so that K becomes smaller as the temperature is increased. (The opposite effect occurs for an endothermic reaction, where heat may be considered a reactant.)

TEST 1.10 Consider the reaction

$$2NO_2(g) \rightleftarrows N_2(g) + 2O_2(g)$$

which is exothermic. A vessel contains $NO_2(g)$, $N_2(g)$, and $O_2(g)$ at equilibrium. Predict how each of the following stresses will affect the equilibrium position.

A. $NO_2(g)$ is added.
B. $N_2(g)$ is removed.
C. The volume is halved.
D. $He(g)$ is added.
E. The temperature is increased.

EXERCISES

1. Give the equilibrium constant expression for each of the following:
   (a) $2H_2(g) + O_2(g) \rightleftarrows 2H_2O(g)$
   (b) $SnO_2(s) + 2H_2(g) \rightleftarrows Sn(s) + 2H_2O(g)$
   (c) $4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(g)$

For exercises 2–5, consider the reaction

$$PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g)$$

2. Write the equilibrium expression.

3. At a certain temperature, the following equilibrium concentrations were observed:

$$[Cl_2] = 2.0 \times 10^{-3} \text{ mol/L}$$
$$[PCl_3] = 3.0 \times 10^{-1} \text{ mol/L}$$
$$[PCl_5] = 6.7 \times 10^{-3} \text{ mol/L}$$

   (a) Calculate the value of K at this temperature.
   (b) Calculate the value of K for the reaction

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$$

   at the same temperature.

4. $Cl_2(g)$, $PCl_3(g)$, and $PCl_5(g)$ are mixed at the following concentrations at the same temperature as in exercise 3:

$$[Cl_2]_0 = 5.0 \times 10^{-4} \text{ mol/L}$$
$$[PCl_3]_0 = 6.3 \times 10^{-2} \text{ mol/L}$$
$$[PCl_5]_0 = 3.8 \times 10^{-3} \text{ mol/L}$$

   In which direction will the system shift to reach equilibrium?

5. $Cl_2(g)$, $PCl_3(g)$, and $PCl_5(g)$ are in a vessel at equilibrium. In which direction will the position of the equilibrium

$$PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g)$$

shift if the total pressure is increased by halving the volume?

6. For the reaction

$$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g)$$

$K = 4.00 \times 10^2$ L/mol at 750°C. What concentration of SO_2 must be in equilibrium with the concentrations $[O_2] = 2.0 \times 10^{-1}$ mol/L and $[SO_3] =$ 3.0 mol/L?

7. The synthesis of ammonia,

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

is exothermic. The value of K for this equilibrium at 600 K is 4.1 $(L/mol)^2$.
(a) Calculate K_p at 600 K.
(b) Will the value of K be larger or smaller than 4.1 $(L/mol)^2$ at 700 K?

For exercises 8 and 9, consider the reaction

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

8. $H_2(g)$ and $I_2(g)$ were mixed at 490°C and allowed to reach equilibrium. The following equilibrium concentrations were found:

$$[H_2] = 2.00 \text{ mol/L}$$
$$[I_2] = 2.49 \times 10^{-2} \text{ mol/L}$$
$$[HI] = 1.50 \text{ mol/L}$$

(a) Calculate K.
(b) Calculate K_p.

9. In another experiment at 490°C, 1.00 mol of H_2, 5.00 mol of I_2, and 2.50 mol of HI were mixed in a 1.00 L vessel. When equilibrium was reached, the concentration of H_2 was found to be 1.00×10^{-1} mol/L. Calculate the equilibrium concentrations of I_2 and HI.

10. Calculate the value of K at 25°C for the reaction

$$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(l)$$

if the *equilibrium* concentrations of $CO_2 = H_2 = CO = 0.10\ M$.

11. Consider the reaction

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$$

for which $K = 8.0 \times 10^{-3}$ mol/L at 750°C.
(a) 1.00 mol of $CaCO_3(s)$ is sealed into a 5.0 L flask at 750°C. Calculate the equilibrium concentration of $CO_2(g)$.
(b) What fraction (by moles) of the original $CaCO_3(s)$ has decomposed?
(c) How many moles of $CaO(s)$ are produced?
(d) Calculate K_p for this reaction at 750°C.

For exercises 12–14, consider the exothermic reaction

$$2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)$$

A study of this system at 25°C found the equilibrium concentrations to be

$$[NO] = 1.0 \times 10^{-3} \text{ mol/L}$$
$$[O_2] = 1.0 \times 10^{-6} \text{ mol/L}$$
$$[NO_2] = 1.3 \text{ mol/L}$$

12. Calculate K at 25°C.

13. Calculate K_p at 25°C.

14. Predict the effect on the equilibrium position of the following stresses:
- (a) Increase the temperature.
- (b) Decrease the pressure by increasing the volume.
- (c) Increase the pressure by adding $Ne(g)$.
- (d) Add 1.0 mol of $O_2(g)$.

15. A 10.0 L flask contains 1.0 mol of $PCl_5(g)$, 0.30 mol of $PCl_3(g)$, and 0.80 mol of $Cl_2(g)$ at equilibrium. Calculate K for the reaction

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$$

16. Consider the reaction

$$2NH_3(g) \rightleftarrows N_2(g) + 3H_2(g)$$

at a temperature where $K = 3.0 \times 10^{-8}$. In an experiment, 1.0×10^{-3} mol NH_3, 1.0×10^{-1} mol H_2, and 1.0 mol N_2 are mixed in a 5.0 L vessel.
- (a) Is this system at equilibrium?
- (b) If not, in which direction must the system shift to reach equilibrium?
- (c) Define the change needed to reach equilibrium in terms of x.
- (d) Represent the equilibrium concentrations in terms of the initial concentrations and x.

17. $N_2O_4(g)$ decomposes to $NO_2(g)$ according to the following equation:

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

Pure $N_2O_4(g)$ was placed in a closed flask at 127°C at a pressure of 4.38×10^{-2} atm. After the system reached equilibrium, the *total* pressure was found to be 7.43×10^{-2} atm. Calculate the value of K_p for this reaction.

Verbalizing General Concepts

Answer the following in your own words.

18. What is chemical equilibrium?

19. How does an equilibrium position differ from an equilibrium constant?

20. What is the reaction quotient and how is it used?

21. What is Le Châtelier's Principle?

22. Using Le Châtelier's Principle, state how a change in volume of the reaction vessel of a system at equilibrium affects the equilibrium position.

23. The addition of an inert gas to a system at equilibrium has no effect. Explain.

Multiple Choice Questions

Questions 24–28 deal with the following equilibrium:

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g) \qquad \Delta H = 125 \text{ kJ}$$

6.0 mol of $PCl_5(g)$ are placed in an empty 10.0 L reaction vessel at 230°C and the reaction is allowed to come to equilibrium. When equilibrium is reached, an analysis of the mixture indicates that 1.0 mol of $Cl_2(g)$ is present.

24. How many moles of $PCl_5(g)$ are present at equilibrium?
- (a) 0.0 mol
- (b) 1.0 mol
- (c) 5.0 mol
- (d) 5.6 mol
- (e) 6.0 mol

25. What is the molar concentration of $Cl_2(g)$ at equilibrium?
   (a) 0.1 mol/L
   (b) 0.2 mol/L
   (c) 0.5 mol/L
   (d) 1.0 mol/L
   (e) 2.0 mol/L

26. The value of the equilibrium constant, K, is
   (a) $\frac{0.1 \times 0.1}{0.5}$
   (b) $\frac{1 \times 1}{5}$
   (c) $\frac{1 \times 1}{6}$
   (d) $\frac{5}{1 \times 1}$
   (e) $\frac{0.5}{0.1 \times 0.1}$

27. The numerical value of the equilibrium constant, K, for this reaction may be expected to
   (a) Increase as temperature is increased to 250°C and pressure is held constant.
   (b) Increase as pressure is increased and temperature is held constant.
   (c) Increase if some additional Cl_2 is injected, temperature and pressure being held constant.
   (d) Remain unchanged no matter how conditions are altered.

28. Which of the following would surely increase the amount of $PCl_3(g)$ present at equilibrium?
   (a) Decrease the volume at constant temperature.
   (b) Inject some $Cl_2(g)$ into the system at equilibrium.
   (c) Decrease the temperature at constant pressure.
   (d) Remove some $PCl_5(g)$ from the system at equilibrium.
   (e) Inject some $PCl_5(g)$ into the system at equilibrium.

29. Calculate the equilibrium constant, K_p for the following reaction:

$$2NOBr(g) \rightleftarrows 2NO(g) + Br_2(g)$$

given that a 1.0 L vessel was initially filled with 4.0 atm of pure NOBr, and after equilibrium was established, the partial pressure of NOBr gas was 2.5 atm.
   (a) 0.45
   (b) 0.27
   (c) 0.18
   (d) 0.75
   (e) None of these

30. After equilibrium has been attained in the reaction system in question 29, decreasing the total pressure (by increasing the volume) will result in
   (a) An increase in the equilibrium constant.
   (b) A decrease in the equilibrium constant.
   (c) A shift of the equilibrium position to the right.
   (d) A shift of the equilibrium position to the left.
   (e) None of these.

31. In the reaction

$$C(s) + CO_2(g) \xrightleftharpoons{1000\ K} 2CO(g)$$

if one mole of solid carbon is added to the system at equilibrium, the result when equilibrium is reattained will be
   (a) To increase the quantity of CO by 2 mol.
   (b) To decrease the quantity of CO by 2 mol.
   (c) No change.
   (d) None of these.

For questions 32–35, consider the reaction

$$Fe_2O_3(s) + 3H_2(g) \rightleftarrows 2Fe(s) + 3H_2O(g) \qquad \Delta H^\circ = 15\text{ kJ}$$

32. The equilibrium expression is

(a) $K = \dfrac{[Fe]^2[H_2O]^3}{[Fe_2O_3][H_2]^3}$ (b) $K = \dfrac{1}{[H_2]^3}$

(c) $K = \dfrac{[H_2O]^3}{[H_2]^3}$ (d) None of these

33. The equilibrium concentrations under certain conditions were found to be

$$[H_2O] = 1.0\text{ mol/L}$$
$$[H_2] = 2.5\text{ mol/L}$$

Calculate K.

(a) 0.40 (b) 0.064

(c) 15.6 (d) Insufficient information to calculate

34. K_p is

(a) Less than K (b) Greater than K

(c) Equal to K (d) Insufficient information to predict

35. Use the following choices:

(a) Shift left (b) Shift right

(c) No change (d) Not possible to predict

to indicate the effect of each of the following stresses on the position of this system at equilibrium:

(1) Decrease the volume of the container.

(2) Add $Fe_2O_3(s)$.

(3) Remove $H_2O(g)$.

(4) Increase the temperature.

36. For the reaction

$$4NH_3(g) + 5O_2(g) \rightleftarrows 4NO(g) + 6H_2O(g)$$

ΔH° is negative. The position of this equilibrium would be shifted to the left by

(a) Removing $NO(g)$.

(b) Adding $O_2(g)$.

(c) Increasing the pressure by decreasing the volume of the container.

(d) Decreasing the temperature.

(e) None of these.

37. Calculate the equilibrium constant for the following reaction:

$$2A(g) \rightleftarrows B(g) + 3C(g)$$

given that a 1.0 L vessel was initially filled with 5.0 atm of pure A and the partial pressure of gas A was found to be 3.5 atm at equilibrium.

(a) 1.1 atm^2 (b) 0.70 atm^2

(c) 3.8 atm^2 (d) 0.48 atm^2

(e) None of these

38. Increasing the volume of the reaction vessel in question 37 would have what effect?

(a) Increase the equilibrium constant.

(b) Force the reaction to proceed to the right.

(c) Force the product ratio [C]/[B] to be greater than 3.
(d) Only (a) and (b) are correct.
(e) (a), (b), and (c) are correct.

39. Consider the following equilibrium system:

$$SnCl_2(s) + Cl_2(g) \rightleftarrows SnCl_4(l) + 195\text{ kJ}$$

The position of this equilibrium could be driven to the *right* by
(a) Compressing the system in the reaction chamber.
(b) Increasing the temperature in the reaction chamber.
(c) Adding more $SnCl_4(l)$ to the reaction mixture.
(d) Adding more $SnCl_2(s)$ to the reaction mixture.
(e) All of the above would drive the reaction farther to the right.

40. Given the following equation:

$$A + B \rightleftarrows 3C + D$$

where initial concentrations of A and B are each equal to 1.2 mol/L with no C or D present. At equilibrium, the concentration D is found to be 0.30 mol/L. Calculate K.
(a) 0.27
(b) 0.33
(c) 0.010
(d) 0.030
(e) None of these

41. For the gas phase oxidation of CO to CO_2 by means of O_2:

$$2CO + O_2 \rightleftarrows 2CO_2$$

the equilibrium constant expression is
(a) $K = \frac{[CO_2]^2}{[CO][O_2]}$
(b) $K = \frac{[CO_2]^2}{[CO]^2[O_2]}$
(c) $K = \frac{[CO]^2[O_2]}{[CO_2]}$
(d) $K = \frac{[CO]^2[O_2]}{[CO_2]^2}$
(e) $K = \frac{[CO][O_2]}{[CO_2]}$

42. Two moles of NH_3 gas are introduced into a previously evacuated 1.0 L container in which it partially dissociates at high temperature:

$$2NH_3(g) \rightleftarrows N_2(g) + 3H_2(g)$$

At equilibrium, 1.0 mol of $NH_3(g)$ remains. What is the equilibrium constant for the above reaction?
(a) 0.42
(b) 0.75
(c) 1.5
(d) 1.7
(e) None of these

43. Which of the following affects the *value* of K for gaseous reactions?
(a) Change in pressure of reactants or products.
(b) Change in concentration of reactants or products.
(c) Change in temperature.
(d) Change of volume of the container.
(e) None of these.

For questions 44–48, consider the equilibrium

$$H_2O(g) + CO(g) \rightleftarrows H_2(g) + CO_2(g) \qquad \Delta H^\circ = -40\text{ kJ}$$

Use the following choices
(a) Shift to the right
(b) Shift to the left
(c) No change
(d) Not enough information to predict

to give the effect of each of the following stresses on the position of the equilibrium for this reaction:

44. 1.0 mol of $H_2(g)$ is added.

45. 1.0 mol of $CO(g)$ is removed.

46. 1.0 mol of $He(g)$ is added.

47. The pressure is doubled by halving the volume.

48. The temperature is decreased.

49. In which reaction will a decrease in volume at constant temperature favor formation of the products?
(a) $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$ (b) $H_2(g) + Cl_2(g) \rightleftarrows 2HCl(g)$
(c) $2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)$ (d) $COCl_2(g) \rightleftarrows CO(g) + Cl_2(g)$

50. Given the equilibrium equation

$$A_2(g) + B_2(g) \rightleftarrows 2AB(g)$$

where the equilibrium concentrations in mol/L are

$$[A_2] = 0.40$$
$$[B_2] = 0.40$$
$$[AB] = 1.20$$

what is the value of the equilibrium constant?
(a) 0.11 (b) 0.13
(c) 1.8 (d) 9.0

51. For the equilibrium system $N_2(g) + 2O_2(g) \rightleftarrows 2NO_2(g)$, where the forward reaction is endothermic, which of the following statements is *not* true?
(a) A decrease in volume will shift the position of the equilibrium to the right.
(b) An increase in temperature will shift the equilibrium to the left.
(c) The equilibrium expression is $K = [NO_2]^2/[N_2][O_2]^2$
(d) A decrease in the concentration of N_2 will shift the position of the equilibrium to the left.

52. For the reaction $2CO(g) + O_2(g) \rightleftarrows 2CO_2(g)$, the initial concentrations for CO, O_2, and CO_2 are each 0.10 mol/L. $K = 4 \times 10^{-16}$ at 500°C. To establish equilibrium, the system will
(a) Proceed to the right. (b) Proceed to the left.
(c) Not change. (d) Cannot tell; insufficient information.

53. The equilibrium constants K_I and K_{II} for the reactions

$$\text{I. } N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$
$$\text{II. } \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftarrows NH_3(g)$$

are related as
(a) $K_I = K_{II}$ (b) $K_I = \frac{1}{K_{II}}$
(c) $K_{II} = \sqrt{K_I}$ (d) $K_I = \sqrt{K_{II}}$
(e) None of these

Note: The following exercises require the solution of quadratic equations.

54. Consider the reaction

$$PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g)$$

at a temperature where $K = 11$ L/mol. If 1.0×10^{-3} mol of $Cl_2(g)$, 1.26×10^{-1} mol $PCl_3(g)$, and 7.6×10^{-3} mol of $PCl_5(g)$ are mixed in a 2.0 L vessel, calculate the equilibrium concentrations of $Cl_2(g)$, $PCl_3(g)$, $PCl_5(g)$.

55. 1.00 mol of $N_2O_4(g)$ is placed in a 10.0 L vessel and allowed to reach equilibrium. The reaction of interest is

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

where $K = 8.1 \times 10^{-2}$ mol/L. Calculate the equilibrium concentrations of $N_2O_4(g)$ and $NO_2(g)$.

For questions 56 and 57, consider the reaction

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

where $K_p = 1.7 \times 10^{-3}$ atm^{-2} at 600 K.

56. 0.10 atm of N_2 is mixed with 0.50 atm of H_2 in a 1.0 L flask at 600 K. Calculate the equilibrium pressures of $N_2(g)$, $H_2(g)$, and $NH_3(g)$.

57. 0.0200 atm of $H_2(g)$, 0.0800 atm of $N_2(g)$, and 0.100 atm of $NH_3(g)$ are placed in a 1.00 L flask at 600 K.
(a) In which direction will the system shift to come to equilibrium?
(b) Calculate the equilibrium pressures of $N_2(g)$, $H_2(g)$, and $NH_3(g)$.

For questions 58 and 59, consider the reaction

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

at a temperature where $K = 38.6$.

58. 1.800 mol of H_2, 1.800 mol of I_2, and 2.600 mol of HI are mixed in a 2.000 L vessel. Calculate the equilibrium concentrations of H_2, I_2, and HI.

59. 1.00 mol of I_2 is added to the system at equilibrium in question 58.
(a) In which direction does the position of the equilibrium shift?
(b) Calculate the new equilibrium concentrations.

60. Consider the equilibrium mixture from question 15. Now 1.00 mol of $PCl_5(g)$ is added to this mixture in the 10.0 L vessel. Calculate the new equilibrium concentrations of Cl_2, PCl_3, and PCl_5.

61. Consider the reaction

$$2HI(g) \rightleftarrows H_2(g) + I_2(g)$$

at 620°C where $K = 1.63 \times 10^{-3}$. In an experiment, 0.600 mol of $H_2(g)$, 0.300 mol of $I_2(g)$, and 0.800 mol of $HI(g)$ are added to a 2.0 L vessel. Calculate the equilibrium concentrations of HI, H_2, and I_2.

62. Consider the reaction

$$2ClO(g) \rightleftarrows Cl_2(g) + O_2(g)$$

at a temperature where $K = 6.4 \times 10^{-3}$. In an experiment, 1.00×10^{-1} mol of $ClO(g)$, 1.00 mol of $O_2(g)$, and 1.00×10^{-2} mol of $Cl_2(g)$ were mixed in a 4.00 L flask.
(a) Is the system at equilibrium?
(b) If not, in which direction must the system proceed to reach equilibrium?
(c) Calculate the concentrations of $ClO(g)$, $Cl_2(g)$, and $O_2(g)$ at equilibrium.